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Ab-initio study of optical conductivity of B_xC_y nano-composite system

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Abstract : We compute the imaginary part of the dielectric constant $\epsilon_2(q \to 0, \omega)$ of Single Wall Carbon Nanotubes (SWCNTs) alloyed with Boron (B) through fixed C–C bond length *ab-initio* Density Functional Theory (DFT) It is observed that the dielectric constants (both real as well as imaginary) essentially depend on B-doping concentration as well as the direction of polarization In particular, we demonstrate that the maximum value of the optical conductivity of this composite system depends strongly on the B-concentration in a *non-linear* way with a *unique minimum* at a particular critical concentration This study may be of importance in discussing the nature of collective excitations in B-alloyed SWCNT system

Keywords : Optical conductivity, Nano Composite System, *ab-initio* calculation

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1. Introduction

Recent years have seen considerable advancement in research in C_{60} and carbon nanotubes [1,2]. It is well known that the intrinsic carbon nanotubes are unable to detect the highly toxic gases, water molecules and bio-molecules [3]. To improve the nanosensor reliability as well as quality, the importance of substitutional doping of impurity atoms such as boron, nitrogen atoms have been demonstrated in the literature [4]. Apart from this, an enhancement of electron field emission [5] has been observed in B doped system. In general, through the reaction with B_2O_3 with CNT under Ar atmosphere [6] boron atom/s can be substituted in the carbon atoms/s of SWNT. Recently, electronic structure and optical properties of boron doped single wall carbon nanotubes (SWCNT) have been studied in detail and it is found that boron is in sp^2 configuration [7]. It has been also shown recently that even a small amount dopant can drastically change the mesoscopic conductivity of chemically boron doped carbon nanotubes [8]. All the above examples show the importance of the study of composite nanotubes and invite further investigation about the optical properties of the doped

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system. Since this doping can alter the band structure (such as band gap, the density of states near Fermi energy) considerably [9,10], we would naturally expect some dramatic changes in the response of the B-doped carbon nanotubes under an electromagnetic field. The optical properties of 4 Å diameter pure single wall nanotube have been investigated [11–13] recently by first principles calculation to explain the experimental results.

In this paper, we study the response of the boron doped pure semiconductor carbon nanotube under the action of a uniform electric field with various polarization directions through *ab-initio* calculations with chemical doping of boron in a semiconductor (8,0) nanotube. We finally discuss the variation of optical conductivity as a function B doping concentration in different polarizations as well as un-polarized case.

2. Numerical methods

The optical properties of any system are generally studied by the complex dielectric function defined by

$$\boldsymbol{D}(\omega) = \varepsilon(\omega)\boldsymbol{E}(\omega) = [\varepsilon_1(\omega) + \varepsilon_2(\omega)]\boldsymbol{E}(\omega)\,. \tag{1}$$

However, $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are not independent of each other. If one knows the values of any part for a wide enough range of frequency, then it is possible to get the other one *via* Krammers-Kronig relation. The conductivity $\sigma(\omega)$ is related to the dielectric constant *via* relation

$$\sigma(\omega) = \sigma_1 + i\sigma_2 = \frac{-i\omega}{4\pi}(\varepsilon - 1)\,. \tag{2}$$

We calculate the imaginary part of the dielectric function using first order time dependent perturbation theory as implemented in CASTEP code [14]. For the exchange and correlation term, the Generalized Gradient Approximation (GGA) as proposed by Perdew-Burke-Ernzerhof [15] was adopted. The norm-conserving pseudo-potential in reciprocal space was invoked for the optical calculation. Compared to standard Local Density Approximation (LDA) (with appropriate modifications) used mostly in electronic band structure calculation, the optical properties are standardized by *spin un-polarized* GGA. A cutoff energy of 470 eV for the grid integration was adopted for computing the charge density. We have used 6 Monkhorst [16] *k*-points for Brillouin zone integration along the tube axis. The detailed numerical procedure will be published elsewhere [17]. Geometry optimization of the doped SWNT has not been considered in this short paper.

3. Results and discussion

(A) Study of variation of dielectric function with boron doping :

Before we discuss the optical properties, we show in Figure 1 the typical stick and ball model of (8,0) B_3C system. We compute the imaginary part of the dielectric

constant within the specified frequency range for semiconductor SWCNT. We note that the static value (strictly speaking $\omega \rightarrow 0$, but in our numerical computation ω = 0.0150 Hz) of the dielectric constants for both pure and doped system is always positive. We note that the change of value of static dielectric constant depends on both polarizations as well as on the nature of CNT. The real parts of the static dielectric constant at ω = 0.0150 Hz. for various B concentrations are shown in Figure 2.

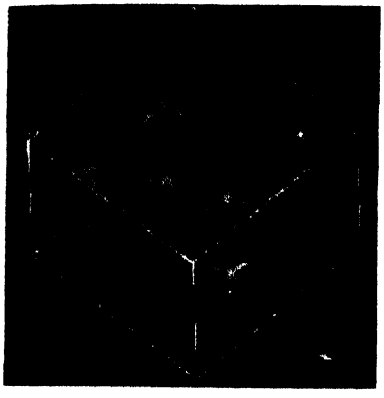

Figure 1. Ball and stick model of (8,0) B_3C tube in 3*d* triclinic structure.

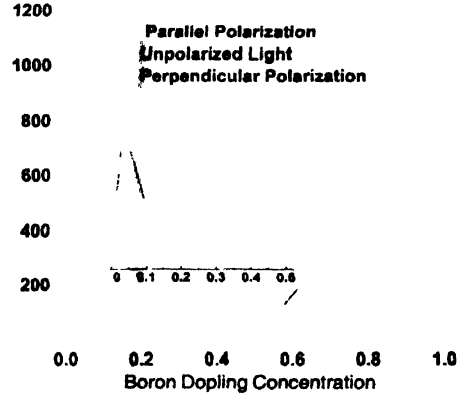

Figure 2. Variation of static (real) dielectric constant of (8,0) B doping for parallel and perpendicular CNT with polarization un-polarized one. Inset shows along with the extended version of the same graph is depicted up to 0.5 doping.

It is evident from the figure that unlike the single B-doped system, for BC_3 tubes (corresponding to 0.25 concentration) in all three cases, the static values (both real as well as imaginary) are increased as compared to pure (8,0) tube. The most remarkable fact is that such a small boron concentration is enough to change the optical behavior drastically in compared to pure case. With increase of boron concentration, the static values decrease and reach very close to pure case. Since boron atom has one 2*p* electron and with increase of boron atom, the system resembles more or less with the pure one. For parallel and un-polarized case, the enhancements of the static values are appreciable at a particular concentration in compared to the perpendicular one. However, at 0.75 and above boron doping, we find a significant giant enhancement of the static dielectric constant for all direction of polarizations including the un-polarized case. This could be due to the availability of large free charge carriers in the system.

(B) Study of the optical conductivity of the doped system :

The optical conductivity is studied from the dielectric constant with zero DC conductivity and 0.5 eV Drude damping. It is noticed that real part of the conductivity σ_1 is always positive throughout the range of the frequency while the imaginary part σ_2 oscillates between the positive and negative values. This feature is common in any direction of electromagnetic field including the un-polarized one. The multiple peaks in lower frequency region in pure (8,0) have been smoothen in B_3C. The maximum value of the

peak in B_3C has been substantially enhanced in compared to pure case. This is due to increase of free electrons in B_3C. Besides, in contrast to pure situation, the peak position in B_3C has been shifted to lower frequency region. In Figure 3, we show the variation of the maximum optical conductivity (both real as well as imaginary) with boron doping concentration for parallel polarization and un-polarized light with incidence (1.0, 0.0, 0.0). A typical polynomial fit suggests the existence of a unique minimum value of $\sigma_{max}(\omega)$ at a particular boron doping concentration in all three cases. The values of the concentration at which the minima occur differ in each case signaling the dependence of the nature of incident electromagnetic field. We show in the following table (Table 1) the typical values of the minima of $\sigma_{max}(\omega)$ and the corresponding doping concentration for three situations.

Table 1. Result of minima of optical conductivity.

Polarization	Minimum value of σ_1^{max}(eV)	Respective boron doping concentration	Minimum value of σ_1^{max}(eV)	Respective boron doping concentration
Paralle 1	0.709	0.421	0.364	0.413
Perpendicular	1.454	0 182	0.734	0.200
Un-polarized	1.225	0.389	0.561	0.382

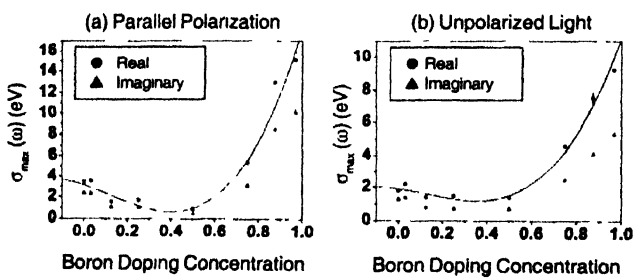

Figure 3. The maximum optical conductivity $\sigma_{max}(\omega)$ as a function of boron doping is shown for (a) parallel polarization, (b) un-polarized light with incidence (1,0,0).

4. Conclusions and perspectives

From the first principles optical study of the b-doped SWCNT (8,0) semiconductor system, we observe that above a certain critical concentration of boron doping, the static values of the dielectric constant are considerably enhanced in compared to pure case. The real as well as the imaginary part of the maximum value of the optical conductivity show a non-linear behavior with boron doping having unique minima in polarized as well as un-polarized cases.

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